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The Autoxidation of Toluene Catalyzed by Metal Ions in Aqueous Solutions. I[*1,*2]

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The yield of benzaldehyde, which was the main product, depended on the kind of metal ions between 100°C and 200°C. The yield was high in a ferrous sulfate solution, even at lower temperatures, while it was extremely low in a ferric sulfate solution, even above 180°C. The yield in a cupric sulfate solution was appreciable at 180°C only with γ-radiation, while it was high near 200°C even without γ-radiation. All the yields were a little higher with γ-radiation than without γ-radiation. The rate-constant ratio of toluene to toluene-d_8 was about 1.4 for the benzaldehyde and benzyl alcohol produced by using Fenton's reagent at 70°C, respectively. It may be concluded from the experiments using the oxygen-18 enriched water that the oxygen of the benzaldehyde produced is transferred from the dissolved molecular oxygen, while that of benzyl alcohol is transferred partly from water. On the basis of these facts, a whole reaction scheme is proposed for the present system. The difference between toluene and benzene is also discussed in the present paper.

The effect of metal ions on the autoxidation of benzene to phenol in an aqueous solution of iron or copper sulfate between 100°C and 200°C had been studied in our laboratory.[1-4] The mechanisms have also been established by using stable isotopes, benzene-d_6, and oxygen-18 enriched water.[5,6] In order to develop the chemistry of the metal-catalyzed autoxidation in an aqueous solution, toluene was also oxidized by the same procedure in the present study. The present main product was benzaldehyde. The findings were somewhat different between toluene and benzene. The autoxidation mechanisms were then confirmed more precisely on the basis of these differences.

Most of the experiments were carried out in a stainless-steel reactor between 100°C and 200°C (procedure A), but some of them were done in a glass flask at 70°C using Fenton's reagent as an initiator (procedure F). All the experiments in the present paper are of the former group unless specially mentioned.

Experimental

Reagents. The aqueous solutions contained ferrous, ferric, or cupric sulfate, dissolved by 0.01 M as metal ions. The oxygen-18-enriched water was obtained from the Weizman Institute of Science, Israel.

The toluene used (Spectrograde reagent of Merck) contained a small amount of impurities, benzene (2.3×10^{-3} M), ethylbenzene (3.6×10^{-4} M), and xylene (1.9×10^{-3} M), according to gas chromatography (PEG 6000, 80°C), but no detectable amount of any compounds with a shorter retention time than benzene. Toluene-d_8, obtained from Merck Sharp & Dohme of Canada, was extremely pure according to gas chromatography and mass-spectrometry.

Oxidation Procedure A. Toluene was oxidized by the same procedure as benzene, a procedure described in the previous paper.[2] That is, 1 cc of toluene was put on 15 cc of the aqueous solution in a hard-glass tube in a 50 cc stainless-steel reactor under an oxygen pressure of 30 atm. This system was then heated by a controlled procedure, and kept for 30 min at a given temperature between 100°C and 200°C. When it was irradiated, a dose of about 16000 R of cobalt-60 gamma rays was given for 25 min.

Oxidation Procedure F. Some runs were initiated by Fenton's reagent for the sake of reference. Ten cubic centimeters of 1.5% hydrogen peroxide aqueous solution was added drop by drop, over a period of about 90 sec, to 100 cc of an 0.4 N sulfuric acid solution containing 0.01 M ferrous sulfate, in which 1 cc of toluene had been suspended by a magnetic stirrer.[6] Then, after they had been stirred for 5 min and cooled, the products were extracted by ether and analyzed by gas chromatography.

The toluene mixture used for the experiment on the isotope effect contained about 43% of toluene-d_8. For the experiment on oxygen-18, ferrous sulfate was dissolved in the oxygen-18-enriched water containing

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[*1] Thermal and Radiation Oxidations of Benzene to Phenol in Aqueous Solutions Containing Metal Ions at Elevated Temperatures. X.

[*2] Presented in part at the 17th Symposium on Organic Reaction Mechanisms, Tokyo, October, 1966.

1) H. Hotta and N. Suzuki, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **86**, 651 (1965).

2) H. Hotta, A. Terakawa, K. Shimada and N. Suzuki, This Bulletin, **36**, 721 (1963).

3) H. Hotta, N. Suzuki and A. Terakawa, *ibid.*, **36**, 1255 (1963).

4) N. Suzuki and H. Hotta, *ibid.*, **37**, 244 (1964).

5) H. Hotta, N. Suzuki and T. Abe, *ibid.*, **39**, 417 (1966).

6) H. Hotta, *ibid.*, **40**, 687 (1967).

0.4 N sulfuric acid, and 30% hydrogen peroxide was diluted to 1.5% by the enriched water. For these experiments, the products were separated by gas chromatography at 160°C, and their isotopic compositions were directly analyzed by mass-spectrometry.

Analytical. For procedure A, after the reactor had been cooled, the products in the toluene and aqueous phases were analyzed separately by gas chromatography using a PEG 6000 column at 80°C for acetaldehyde and acetone, one at 150°C for benzaldehyde, and one at 185°C for benzyl alcohol, *o*-, and *p*-cresol. Benzoic acid was examined by using a column of Silicone Gum Rubber-Methyl G. E. S. E. 30 on Diatoport S. The methods used for the analysis of inorganic species were the same as in the previous studies.2,3)

Results

The Yield of Benzaldehyde. In Fig. 1, the total amounts of benzaldehyde produced in the aqueous solutions of ferrous (⊙ and ●), ferric (◬ and ▲), and cupric (⊡ and ■) sulfates, with (open marks) and without (solid marks) γ-radiation, are plotted against the reaction temperature. The amounts of benzaldehyde produced, dissolved in the toluene and aqueous phases respectively, show that the distribution ratio per unit volume in the former to that in the latter is about 100 : 2. This is in contrast to the fact that most of the phenol produced from benzene is in the aqueous phase.

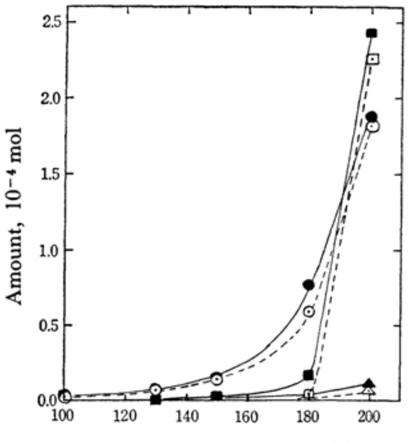

Fig. 1. Amounts of benzaldehyde produced in 0.01 M solutions.

	Irradiated	Unirradiated
$FeSO_4$	●	⊙
$Fe_2(SO_4)_3$	▲	◬
$CuSO_4$	■	⊡

The findings in Fig. 1 show almost the similar tendency as in the benzene oxidation,1-4) but they show some differences between toluene and benzene. The yield of the main product (benzaldehyde or phenol) is generally lower for toluene than for benzene. Especially, the oxidation in the ferric solution is not so much promoted by γ-radiation for toluene as for benzene.4) The yield of benzaldehyde, unlike that of phenol, is not saturated even near 200°C.

The Ferrous Content After Reaction. The concentrations of ferrous (⊙) and ferric (●) species dissolved in the aqueous phase after the reaction at 180°C are shown in Fig. 2 for the unirradiated ferrous solution and in Fig. 3 for the irradiated ferric solution. They were measured for the samples obtained by the experimentation shown in Fig. 1. The percentage of the ferrous species is also shown by crosses in Figs. 2 and 3; these figures indicate that the reduction of iron species occurs with the toluene oxidation.

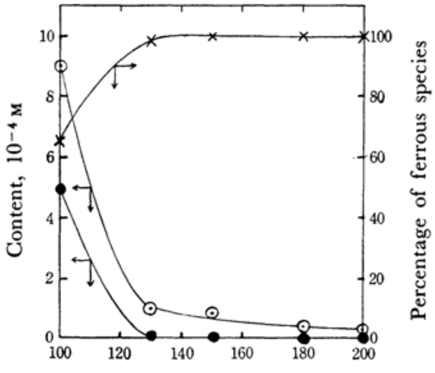

Fig. 2. Contents of ferrous (⊙) and ferric (●) species in the unirradiated ferrous sulfate solution after oxidation at 180°C in Fig. 1.

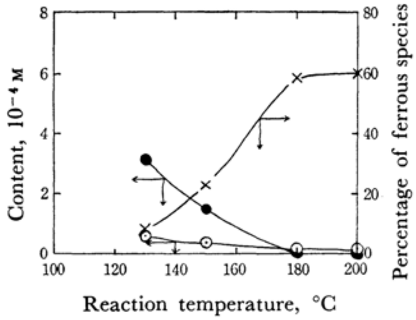

Fig. 3. Contents of ferrous (⊙) and ferric (●) species in the irradiated ferric sulfate solution after oxidation at 180°C in Fig. 1.

The Amount of Toluene Added. In order to determine the optimum volume ratio of toluene to the aqueous solution, the amount of toluene added to the unirradiated ferrous solution was changed from 0.13 to 4 cc, the amount of benzaldehyde produced at 180°C being measured separately for the toluene (⊙) and aqueous (●) phases, as is shown in Fig. 4. Since it was difficult to measure accurately the amount of the

Table 1. Yields of by-products, 10^{-5} mol

Sulfate added	$FeSO_4$		$FeSO_4$		$CuSO_4$	
Temperature, °C	180		200		200	
Phase dissolved	Toluene	Water	Toluene	Water	Toluene	Water
Products						
Benzaldehyde	5.9	Trace	14.7	3.5	17.8	4.9
Benzyl alcohol	0.2	Trace	0.2	2.1	Trace	0
Acetaldehyde	0	Trace	0	0.2	0	0.5
Acetone	0	Trace	0	0.4	0	0.4
Benzoic acid	Less than 0.5					
Cresol	Less than 0.4					

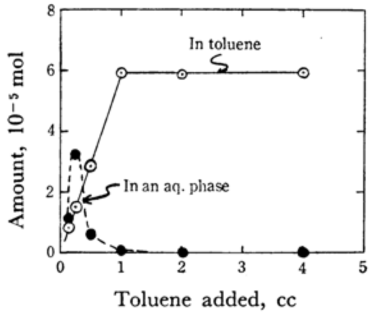

Fig. 4. Amounts of benzaldehyde produced in the unirradiated ferrous sulfate solution at 180°C, detected in the toluene (⊙) and aqueous (●) phases.

residual toluene in a glass tube after reaction when less than 1 cc of toluene was added, the amount of the product in toluene could not be estimated accurately for them, but the amount in the aqueous phase could be reliably determined in such cases. At any rate, the findings in Fig. 4 indicate that 1 cc of toluene per 15 cc of the aqueous solution is enough to extract most of the benzaldehyde produced, as well as to give the reactant.

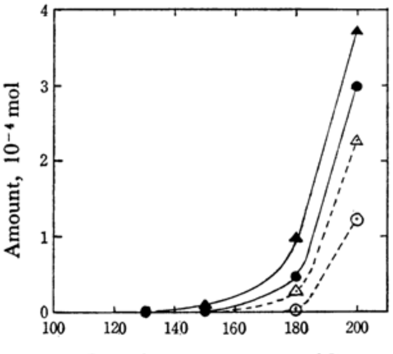

Fig. 5. Amounts of benzaldehyde produced at 200°C in aqueous solutions containing copper pieces (2 g); a) distilled water (⊙), b) 0.01 N sulfuric acid (△), c) 0.01 M cupric sulfate (●) and d) a 0.01 M cupric sulfate solution of 0.01 N sulfuric acid (▲).

The Effect of Added Copper Metal. The oxidation was carried out in the following aqueous solutions, each containing 2 g of copper metal pieces; a) distilled water, b) 0.01 N sulfuric acid, c) an 0.01 M cupric sulfate aqueous solution, and d) an 0.01 M cupric sulfate solution of 0.01 N sulfuric acid. The yields are shown in Fig. 5. The amounts of copper metal dissolved in the aqueous phase after the reaction were 3.4, 9.3, and 11.5×10^{-5} mol at 200°C for the a, b, and d runs respectively. These amounts were almost independent of the temperature. 1.5×10^{-4} mol corresponds to 15 cc of an 0.01 M solution. The production of benzaldehyde is promoted by dissolving copper metal, but the effect is not as sensitive as on the benzene oxidation.[3]

By-products. The amounts of by-products are shown in Table 1 for the samples obtained in several of the unirradiated cases in Fig. 1. These by-products could not be detected by gas chromatography when less than 5×10^{-5} mol of benzaldehyde was produced (*cf.* Fig. 1). This shows that all the products except benzaldehyde are present in trivial amounts when procedure A is used.

On the other hand, the oxidation initiated by Fenton's reagent (procedure F), which gave various products, was in great contrast to the results of procedure A. Although the yields of the products in this case depended on the stirring condition, the dropping rate, *etc.*, the typical results at

Table 2. Result of Fenton's reagent

Product	Relative mole ratio
Unknown A	2.4
Unknown B	0.9
Benzaldehyde	100
o-Hydroxybenzaldehyde	17
Benzyl alcohol	31
o-Cresol	5.5
m- and *p*-Cresols	0.8
Dibenzyl	112
Benzoic acid	Not detected

TABLE 3. CONTENTS OF OXYGEN-18

No.	^{18}O-atom %	Temp., °C	Solvent	Procedure
		a) Benzaldehyde from toluene		
1	0.37	200	$FeSO_4$ soln.	A
2	0.45	200	$CuSO_4$ soln.	A
3	0.62	70	$FeSO_4$ soln., 0.4 N H_2SO_4	F
4	0.88	70	$FeSO_4$ soln., 0.4 N H_2SO_4	B for 30 min
5	0.68	70	H_2O	B for 30 min
		b) Benzyl alcohol from toluene		
6	0.26	70	$FeSO_4$ soln., 0.4 N H_2SO_4	F
7	0.21	70	$FeSO_4$ soln., 0.4 N H_2SO_4	B for 5 min
8	0.20	70	H_2O	B for 5 min
		c) Phenol from benzene		
9	1.06	70	$FeSO_4$ soln., 0.4 N H_2SO_4	F
10	0.48	150	$FeSO_4$ soln.	A⁵⁾
11	0.90	180	$FeSO_4$ soln.	A⁵⁾

Note: See text for procedures A, F and B.

70°C were as shown in Table 2. The yields were higher in an 0.4 N acidic solution than in an 0.01 N acidic solution.

The Content of Oxygen-18. The contents of oxygen-18 in benzaldehyde and benzyl alcohol, which were produced or treated in the unirradiated solutions of the oxygen-18-enriched water (1.72 ^{18}O atom percent) by the following procedures, are shown in Table 3. Procedures A and F are described in detail in the Experimental Section. Procedure B means that 0.2 cc of benzaldehyde or benzyl alcohol was kept in the aqueous phase at 70°C for 5 min or for 30 min without hydrogen peroxide, using the same method as in procedure F. Five minutes corresponds to the stirring at 70°C in procedure F, and 30 min, to the time at an elevated temperature in the reactor in procedure A. Since these samples were directly analyzed by mass-spectrometry without being coverted to carbon dioxide after separation by gas chromatography, the present values are not so accurate as the previous values5) determined by Rittenburg and Ponticorvo's method.7)

Discussion

The following reaction mechanism can be assumed for the autoxidation of toluene, with reference to that of benzene.1-6) In the present paper, M^+ represents a ferrous or cuprous ion, M^{2+}, a ferric or cupric ion, and Ph, a phenyl group (C_6H_5).

Initiation Process. The findings show that the chain process is initiated by the formation of hydroxyl radicals through the following processes.1,2) The radiolysis of an oxygenated aqueous solution gives hydroxyl radicals, as usual;

$$H_2O \rightsquigarrow e_{aq}^-,\ H,\ \cdot OH,\ H_2,\ H_2O_2 \qquad (1)$$

$$e_{aq}^-,\ H \text{ or } H_2O_2 \xrightarrow{O_2,\ M^+} \cdot OH \qquad (2)$$

Even in an unirradiated solution, hydroxyl radicals are given in the presence of M^+ through the reactions:8,9)

$$M^+ + O_2 + H^+ \rightarrow HO_2 + M^{2+} \qquad (3)$$

or, in a neutral solution;

$$M^+ + O_2 \xrightarrow{H_2O} \cdot OH + OH^- + M^{2+} \qquad (4)$$

These hydroxyl radicals react with toluene to give benzyl peroxides in the presence of oxygen:

$$PhCH_3 + \cdot OH + O_2 \rightarrow \text{Peroxide } (RO_2\cdot) \qquad (5)$$

Reaction (5) seems to suggest the hydrogen abstraction of the hydroxyl radical from toluene, followed by the oxidation of the benzyl radical to benzyl peroxide. However, according to Dorfman *et al.*,10) the rate constants of the reaction with the hydroxyl radical at 25°C are $(3.3\pm0.8)\times10^9\cdot$ $M^{-1}\,sec^{-1}$ for benzene and $(3.0\pm0.7)\times10^9\ M^{-1}\,sec^{-1}$ for toluene, in spite of the dissociation energy of the $PhCH_2$–H bond (85 kcal/mol) being lower than that of the Ph–H bond (104 kcal/mol).11) They concluded from this finding that the addition reaction of the hydroxyl radical to the ring occurs primarily even for toluene at 25°C. Anbar *et al.* also support this conclusion.12) In this case, the peroxide ($RO_2\cdot$) produced by reaction (5) is not necessarily benzyl peroxide. However, it is expected that the rate of the abstraction reaction

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7) D. Rittenburg and L. Ponticorvo, *J. Appl. Rad. Isotopes,* **1**, 208 (1956).

8) A. M. Posner, *Trans. Faraday Soc.*, **49**, 382 (1953).

9) G. Czapski and L. M. Dorfman, *J. Phys. Chem.*, **68**, 1169 (1964).

10) L. M. Dorfman, I. A. Taub and D. A. Harter, *J. Chem. Phys.*, **41**, 2954 (1964).

11) J. A. Kerr, *Chem. Revs.*, **66**, 465 (1966).

12) M. Anbar, D. Meyerstein and P. Neta, *J. Phys. Chem.*, **70**, 2660 (1966).

exceeds that of the addition reaction at elevated temperatures.[13,14] The results of Dorfman *et al.* do not give any evidence that such an addition reaction is still predominant over the abstraction reaction at elevated temperatures.

On the other hand, the main products from toluene are the derivatives at the methyl group at 25°C[15] and also at elevated temperatures, as Tables 1 and 2 show. These findings seem, therefore, to support the hydrogen abstraction reaction from the methyl group. However, since most of the products are formed not by the initiation process but by the propagation process, they may give evidence for the following propagation process rather than provide objections against the above suggestion of the addition reaction to the ring.

It is difficult to decide precisely at the present time whether reaction (5) is naturally the addition reaction or the abstraction reaction. Charles and Whittle suggest the possibility of abstraction after addition rather than direct-abstraction.[16] At any rate, it is assumed now that in reaction (5) some peroxide, not necessarily benzyl peroxide, is formed as a result of the initiation process.

Propagation Process. Starting from the peroxide formed by reaction (5), toluene is oxidized consecutively in the presence of metal ions as follows:

$$RO_2\cdot + PhCH_3 \rightarrow RO_2H + PhCH_2\cdot \qquad (6)$$

$$PhCH_2\cdot + O_2 \rightarrow PhCH_2O_2\cdot \qquad (7)$$

$$PhCH_2O_2\cdot + PhCH_3 \rightarrow PhCH_2O_2H + PhCH_2\cdot \qquad (8)$$

$$PhCH_2O_2H + M^+ \rightarrow PhCH_2O\cdot + OH^- + M^{2+} \qquad (9)$$

$$PhCH_2O_2H + M^{2+} \rightarrow PhCH_2O_2\cdot + H^+ + M^+ \qquad (10)$$

and partly:

$$2\ PhCH_2O_2\cdot \rightarrow (PhCH_2O)_2 + O_2 \qquad (11)$$

$$\rightarrow 2\ PhCH_2O\cdot \qquad (12)$$

The hydrogen abstraction reaction is assumed to be as reactions (6) and (8). In order to confirm this assumption, the isotope effect of hydrogen or the rate constant ratio was estimated by this equation:

$$\frac{k_H}{k_D} = \frac{(C_6D_5CD_3)}{(C_6H_5CH_3)} \times \frac{(C_6H_5CHO \text{ or } C_6H_5CH_2OH)}{(C_6D_5CDO \text{ or } C_6D_5CD_2OH)} \qquad (i)$$

from the isotopic composition of the product produced by procedure F, where $(C_6D_5CD_3)/(C_6H_5CH_2)$ is the initial ratio of toluene-d_8 to toluene. This method was discussed in detail in a previous paper, and the experiment was carried out carefully as discussed in it.[6]

The values obtained at 70°C were 1.37±0.04 for benzaldehyde and 1.41±0.04 for benzyl alcohol. The value for the oxidation of benzene to phenol under the same conditions is 1.37±0.02 at 70°C. These values support the idea that the hydrogen abstraction reaction occurs in the propagation process at this temperature, as has been discussed in the previous paper.[6]

In spite of the large difference in bond dissociation energy between toluene and benzene pointed out already, the above values of k_H/k_D are not so different between them, and they are both low in comparison with the usual value for the abstraction reaction.[17] The former fact suggests that these products (benzaldehyde, benzyl alcohol, and phenol) are formed through a similar process, and that there is no hydrogen abstraction reaction except in this step. The latter fact suggests not only that the hydrogen abstraction reaction by peroxides has a low activation energy,[17] but also that reaction (5) may be the addition reaction, as has been discussed already.

The high yield of dibenzyl in Table 2 suggests that the benzyl radical is formed in a high yield; this is, it supports reaction (8). On the other hand, hardly any dibenzyl is produced by procedure A. This is due to the high concentration of oxygen dissolved in the aqueous phase under the high oxygen pressure; all the benzyl radicals can combine with oxygen before they combine with each other.

Termination Process. As seen may be in Figs. 2 and 3, the iron species dissolved in the aqueous phase are reduced to ferrous as benzaldehyde is formed. Therefore, it is assumed to be formed by the reaction:

$$PhCH_2O\cdot + M^{2+} \rightarrow PhCHO + H^+ + M^+ \qquad (13)$$

after reaction (9). Reactions (9) and (13) may be summarized as:

$$PhCH_2O_2H + M^+ \rightarrow PhCHO + H_2O + M^+ \qquad (14)$$

so that benzaldehyde is formed without the oxidation of a metal ion on catalyzed by M^+.

In Table 3 a), oxygen-18 is enriched in the benzaldehyde produced in Experiments 1 and 2, but the oxygen-18-atom percentages are lower than those of Experiments 4 and 5, which showed

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[13] T. Ikawa, T. Fukushima, M. Muto and T. Yanagihara, *Can. J. Chem.*, **44**, 1817 (1966).

[14] N. N. Semenov, "Some Problems of Chemical Kinetics and Reactivity," Vol. I, Pergamon Press, Princeton, N. J. (1958), p. 52.

[15] J. R. L. Smith and R. O. C. Norman, *J. Chem. Soc.*, **1963**, 2897.

[16] S. W. Charles and E. Whittle, *Trans. Faraday Soc.*, **56**, 794 (1960).

[17] K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

that benzaldehyde exchanges oxygen with water at a fast rate even at 70°C.[18] This fact suggests that the oxygen of benzaldehyde produced is transferred not from water during the oxidation process, but from gasesous oxygen dissolved as assumed in reactions (7) and (14).

In Table 3 b), oxygen-18 is enriched to some extent in the benzyl alcohol produced by procedure F (Experiment 6), while benzyl alcohol does not exchange oxygen appreciably with water, as may be seen in Experiments 7 and 8.[18] Therefore, it may be concluded that the oxygen of benzyl alcohol is given partly by water and partly by molecular oxygen dissolved during the oxidation process. Thus, as has been discussed in a previous paper[5] in connection with the oxidation of benzene to phenol, it may be assumed that there are two paths for its formation;

$$PhCH_2O\cdot + M^+ + H^+ \rightarrow PhCH_2OH + M^{2+} \quad (15)$$

$$PhCH_2O_2\cdot + M^{2+} + O^*H^- \rightarrow PhCH_2O^*H + M^+ + O_2 \quad (16)$$

after reactions (9) and (10) respectively, where O* represents an oxygen atom of water. The excess oxygen-18 in Experiment 6 is very small. This shows that the main process is reaction (15), which is competitive with reaction (13). As may be seen in Tables 1 and 2, hardly any benzyl alcohol is produced by procedure A at elevated temperatures in spite of the high yield of procedure F at 70°C. Since the competitive reactions (13) and (15) may be affected by the concentration of metal ions, hydrogen ions or oxygen as well as by the reaction temperature, it is not clear which is the main reason for this difference.

In Table 3 c), the oxygen-18-atom percentage in the phenol produced by procedure F (Experiment 9) is much higher than in the benzyl alcohol produced by the same procedure (Experiment 6). This suggests that the molecular detachment of oxygen from peroxide by the reduction of the metal ion is fast from the ring;

$$PhO_2\cdot + M^{2+} + O^*H \rightarrow PhO^*H + M^+ + O_2 \quad (17)$$

but slow from the side chain (reaction (16)). This difference may be due to the difference in resonance energy between the intermediate ions, the phenyl and benzyl ions.

Although benzaldehyde was produced from benzyl alcohol by procedure A, the rate was not as very fast, even at 200°C, as it was at all consumed, as may be seen in Table 1. If benzaldehyde is formed from toluene through this process, since oxygen-18 is enriched to some extent in the benzyl alcohol produced, as may be seen in Table 3 b), the oxygen-18-atom percentage should be higher than that of Experiment 5, unlike those of Experiments 1 and 2. Therefore, it may be concluded that benzaldehyde is formed not through benzyl alcohol, but through the benzoxy radical, as is assumed in reaction (13).

The Effect of Metal Ions. In Fig. 1, the yield of benzaldehyde is a little higher in the irradiated solutions than in the unirradiated solutions. Especially, hardly any benzaldehyde is produced below 180°C in the unirradiated curpic solution, in contrast to its irradiated solution. This suggests that reaction (1) initiates the chain process. On the other hand, the chain process is promoted in the presence of M^+, as is seen in the ferrous solution (Fig. 1) and upon the addition of copper metal pieces[3] (Fig. 5). This suggests that reactions (3) and (4) are more effective as initiation processes than reaction (1). Furthermore, benzaldehyde is not formed in such a high yield, even in an irradiated aqueous solution without iron sulfate, and iron ions are reduced upon the formation of benzaldehyde, as may be seen in Figs. 2 and 3. These facts cause us to assume reactions (9), (10) and (13) as above.

On the other hand, above 180°C, considerable benzaldehyde is produced even in the solution, in which the formation of the hydroxyl radical is not to be expected from reactions (1)—(4). As has been discussed in a previous paper,[19] in this temperature range, the oxygen of the sulfate group is considerably exchanged with water, and this exchange reaction is promoted in the presence of organic compounds. Furthermore, iron sulafte is decomposed to ferric oxide above 150°C.[20] These facts suggest that sulfur trioxide is present as a transient species in the sulfate solution in this temperature range. Thus, some of this sulfur trioxide is oxidized to the peroxide, which abstracts hydro gen from toluene like reaction (6), instead of the peroxide formed by reaction (5). This assumption was discussed in detail in a previous paper.[19]

The difference between ferric and cupric sulfates in Fig. 1 may be attributed to their concentration at elevated temperatures. The iron concentration in the solution above 180°C is of the order of 10^{-4} M due to the precipitation of ferric oxide,[20] as may be seen in Figs. 2 and 3, while the initial concentration of 10^{-2} M holds in the cupric solution even at this temperature. The yield would decrease considerably in a 10^{-4} M cupric sulfate solution, as in the oxidation of benzene.[4]

Comparison between Toluene and Benzene. When the *G*-value of the product is defined as the

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[18] D. Samuel and B. L. Silver, *Advances in Phys. Org. Chem.*, **3**, 123 (1965).

[19] N. Suzuki, H. Hotta and H. Hashimoto, This Bulletin, **39**, 422 (1966).

[20] H. Hotta and N. Suzuki, *ibid.*, **36**, 717 (1963).

number of molecules per 100 eV of the energy absorbed in 15 g of water, estimated from the difference in the yields between irradiated and unirradiated systems, this value is especially significant for a system in which the yield is negligible if unirradiated. The *G*-values for such systems, namely, the ferric and cupric solutions at 180°C, have been estimated for benzaldehyde from toluene (Fig. 1) and, for the sake of reference, for phenol from the purified benzene,[4] as listed in Table 4.

TABLE 4. *G*-VALUES AT 180°C

Reactant	Toluene	Benzene
Product	Benzaldehyde	Phenol
Sulfate added		
Cupric sulfate	80	160
Ferric sulfate	10	270

As may be seen in Table 4 and Fig. 1, in the ferric solution, the yield of phenol from benzene is high in the solution irradiated at the temperature at which hardly any phenol is produced in the unirradiated solution,[4] while γ-radiation does not promote the oxidation of toluene so much as that of benzene. Although this is not so remarkable in a cupric solution, a similar difference between toluene and benzene is also seen for this case. This fact can be interpreted as follows by the reaction schemes proposed above for toluene and previously for benzene.[2,5]

Benzaldehyde is formed only through the benzoxy radical by reactions (9) and (13), while phenol is formed through the phenoxy radical;

$$PhO_2H + M^+ \rightarrow PhO\cdot + OH^- + M^{2+} \quad (18)$$

$$PhO\cdot + M^+ + H^+ \rightarrow PhOH + M^{2+} \quad (19)$$

and also through phenyl peroxide, which is formed by the reaction

$$Ph\cdot + O_2 \rightarrow PhO_2\cdot \quad (20)$$

or

$$PhO_2H + M^{2+} \rightarrow PhO_2\cdot + H^+ + M^+ \quad (21)$$

(reaction (17)), as had been discussed in a previous paper.[5] The ferric or cupric ion plays an important role in the latter path through phenyl peroxide. It may be concluded from the enrichment of oxygen-18,[5] as is shown in Table 3 c), that the contribution of the latter path to the phenol yield is fairly high, but the reaction corresponding to this path does not occur for toluene, as has been discussed already. It should be remembered in making the interpretation that the concentrations at elevated temperatures are quite different in ferric and in cupric solutions, as has been mentioned above.

This is one of the reasons why the yield of benzaldehyde is not as high as might be expected from the low dissociation energy of the $PhCH_2$-H bond. This does not mean that reaction (10) does not occur, because the chain process in the solution of M^{2+}, especially in a cupric solution, can not be propagated without reaction (10) or (21). Since the content of cuprous ions is negligible as a result of their fast oxidation in the copper sulfate solution,[3] the yield of the product in the irradiated cupric solution in Table 4 can be used as a measure of the rate of reaction (10) or (21). The values in Table 4 show that the rate is faster for benzene than for toluene.

Another possibility may arise from the rate of reactions (7) and (9). It is expected that the rate of reaction (7) is fairly slow, since the benzyl radical is reactiveless as a result of the resonance stabilization,[9,21,22] and that the rate of reaction (18) is much faster than that of reaction (9) due to the resonance stabilization of the phenoxy radical.[23]

When copper metal pieces are added to the aqueous phase, since they supply cuprous ions upon their corrosion, the yield of benzaldehyde becomes high even in the unirradiated solution at the temperature at which it would be low without the addition, as may be seen in Fig. 5. This supports the present initiation mechanism (reactions (3) and (4)). However, the yield does not increase so much as the yield of phenol from benzene.[3] This low yield may also be attributed to the lack of a termination process through the benzoxy radical for toluene, unlike reaction (17) for benzene. The portion of this process to the yield of phenol may be supposed, from the lower enrichment of oxygen-18, to be not so high in the cupric solution as in the ferric solution.[5] However, since the concentration of cupric ions is high as a result of the lack of precipitation, as has been pointed out already, the yield from this process must be fairly high. Furthermore, this process gives cuprous ions, which play important roles in the present reaction scheme, if it occurs.

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